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Controlled release fertilizer based on starch chitosan encapsulation

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Abstract. Phosphor is the main component in a triple super phosphate (TSP) fertilizer which is needed by plants. However, phosphorus is very soluble in the water and makes it easily removed from the soil flowing into the river, and causing algae bloom problems. The solution for the problem is by using the fertilizer coated with starch-chitosan based material. The coated hydrogel bead fertilizer was expected to have a phosphorus controlled-released behaviour and retain the phosphor to be able to stay for a longer time in the soil. This research dealt with studying phosphorus releasing behaviour of starch-chitosan based fertilizer, water uptaking characteristic (swelling), and the morphology of the materials. The commercial granular fertilizer TSP was coated using starch-chitosan suspension. The coatings were conducted by spraying technique. The chitosan-starch mass ratio used were 100:0, 30:70, and 70:30, otherwise the starch percentages were made of 1%, 2%, and 3%. After coated by starch-chitosan suspension, the fertilizers were dried and used on the soil media. The soil which contained coated fertilizer was regularly watered and the phosphorus content was analyzed. The study showed that the water uptaking of the coated fertilizer was higher than that of the conventional uncoated fertilizer. The optimum condition of the chitosan-starch based coating was 30:70 and 2% of starch percentage. Furthermore, the higher chitosan content yielded the higher water uptaking capacity. This phenomenon is supported by the Scanning Electron Microscope (SEM) result. The coating fertilizer with higher chitosan content (ratio of 70:30, 2% starch) had more pores than that of lower chitosan content (ratio of 30:70, 1% starch).

1. Introduction

Phosphorus is the important component in triple super phosphate (TSP) fertilizer. The component is easily dissolved and carried away by water which causes eutrophication problems [1]. According to [2], the phosphorus absorbed by plants is only 10-15% while the rest is released into the waters. This means that fertilizer efficiency is low because a lot of phosphorus is wasted.

Fertilizers can be modified to produce the fertilizer which has slower release behaviour than that of the conventional fertilizer. The purposes of modification are to control the release of nutrients into soil and to prolong the availability of the nutrients in the soil [3].

The modification can be conducted by coating the fertilizer using polymers such as chitosan and starch. Chitosan is a biopolymer which has an amine group produced from deacetylation of chitin and can be extracted from shrimp waste [4]. Besides having controlled release behavior, both chitosan and



starch have the ability to swell (save water). Those characteristics make them have a dual function on fertilizer, as a controlled release system and also as a water storage system that maintains the availability of water in the soil, especially in the dry season.

This study aims to synthesize and characterize chitosan-starch-coated fertilizers. The characterization includes the morphology and swelling properties of coated fertilizers. Then, the performance of coated TSP fertilizers is analyzed by the release rate of the component. The effect of the chitosan : starch mass ratio as coating material is also analyzed.

2. Experimental

The research was carried out in three steps of processes. The steps consist of the synthesis of chitosan-starch coated fertilizers, the characterization of the coated fertilizer, and the analysis and modelling of phosphorus release rate.

2.1. Synthesis of hydrogel bead fertilizer

Chitosan solution 1% (w/w) was prepared by dissolving chitosan powder in 1% (v/v) acetic acid solution. The starch gel was made by heating 1, 2, and 3% (w/v) of tapioca flour in distilled water at 76 °C. Chitosan solution and starch gel with mass ratio (100:0, 70:30, 30:70) were stirred for 30 minutes. Then, the mixture was added 0.8 %w/w citric acid solution as a crosslinking agent and stirred for 2 hours. The coating process was conducted by spraying the coating mixture onto the entire surface of the fertilizer. After that, the coated fertilizer was dried at 60 °C for 12 hours. The fertilizer coating process was repeated for 5 layers.

2.2. Characterization of hydrogel bead fertilizer

The characterization of coated fertilizers was analysed by studying the morphology and the swelling behaviour of the coating system. Morphological analysis was carried out using Scanning Electron Microscope (SEM). The morphology of the coated fertilizer surfaces was observed using an SEM FEI INSPECT S-50, Netherlands. The surface of the fracture was attached onto double-sided carbon tape and subsequently placed in a sample holder.

The swelling analysis was carried out by immersing dry-coated fertilizer samples in water for definite time and then weighing them. The procedure was repeated until the hydrogel bead fertilizers achieved the equilibrium. It was assigned by constant weight of the samples. Furthermore, the swelling parameters were analysed by comparing the changes in the coated fertilizer mass at a certain time to the dry hydrogel mass of coated fertilizer.

2.3. Controlled release of hydrogel bead fertilizer

A certain amount of coated fertilizer and topsoil were placed in a polybag that has been perforated. The arrangement on polybag was placed of soil-coated fertilizer-soil in series. Water reservoir was placed below the polybag to keep the water drain. Furthermore, the analysis was conducted by watering each system with some amount of water for 7 days. After the watering process, the soil sample was analysed using spectrophotometer to find out how much phosphorus was released in the soil. The phosphorus in the sample was quantitatively determined via colorimetry by reacting orthophosphate with ammonium molibdovanadat to form a yellow complex molibdovanadat phosphoric acid compound. Yellow liquid containing phosphorus was analysed by spectrophotometer.

3. Results and Discussions

The commercial TSP fertilizer which has 36 %w/w phosphorus content was increased in its efficiency by modifying the fertilizer. Modification was conducted by coating the fertilizer surface with chitosan-starch mixture. The variation systems consist of 1% chitosan : starch with ratio 100: 0 (A), 70:30 (B), 30:70 (C)- 1% starch and 1% chitosan : starch 70 : 30 with 1% starch(D), 2% starch (E), 3% starch (F) and non-coating fertilizer (G). The phosphorus released in the soil was analysed on the same

treatments for each variations. The optimum results of the variations were analysed on the morphology, swelling ability, and the release rate of phosphorus content.

3.1. Morphology of chitosan-starch coating surface

The morphology of chitosan-starch coating on samples C and E was analyzed by Scanning Electron Microscope (SEM). The samples C and E have the optimum performance on phosphorus release. The C sample was coated fertilizer which has chitosan: starch ratio 30:70 ratio and 1% starch concentration, while sample E was coated fertilizer which has chitosan : starch ratio 70:30 and 2% starch concentration.

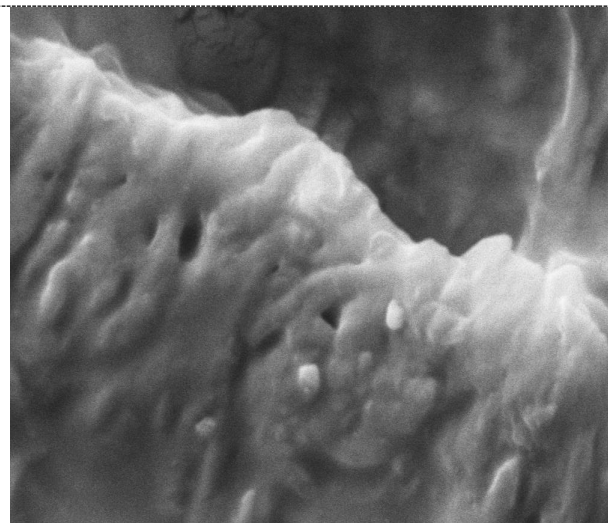


Figure 1. The morphology of coated fertilizer for chitosan : starch ratio 30 : 70 and 1 % starch solution (sample C)

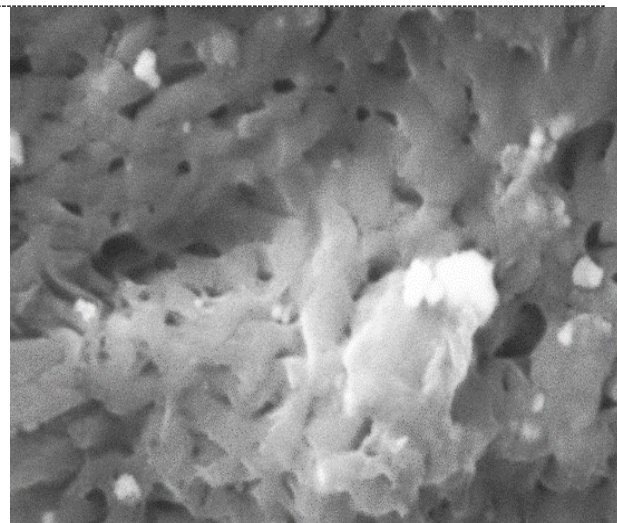
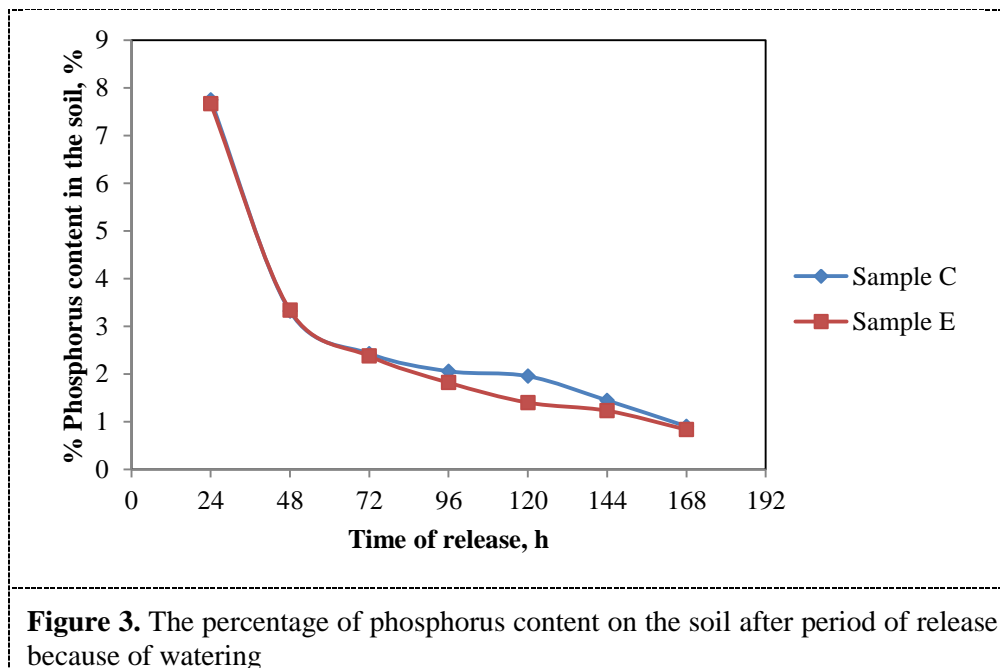


Figure 2. The morphology of coated fertilizer for chitosan : starch ratio 70 : 30 and 2 % starch solution (sample E)

Figure 1 and 2 show that the film coating consists of fiber matrix and some granulars distributed on the matrix. The fiber matrix is chitosan structure while the granular is starch component. The arrangement of chitosan fiber created pores on the film structure. The starch granular was attached on the chitosan matrix by crosslink linkage. The crosslink linkage occurred because the hydroxyl (OH) group in starch was replaced by an amine group (NH₂) from chitosan [5]. The matrix structure with granular became the surface to barrier the phosphorus content of TSP fertilizer release. The sample C (Figure 1) was more dense than the sample E (Figure 2). Sample C had more starch content, whereas the sample E had more chitosan content. An increase in starch content caused the coating pores to become more dense than that of higher chitosan content. The pore size in sample C was 200-300 nm while in sample E was 200-600 nm.

Besides the size of pores on the matrix coating, there were different number of pores for both of the samples. The sample E showed more number of pores than that of sample C. It indicates that sample E is easier to pass phosphorus content than that of sample C. This is proven by the amount of phosphorus on the soil for period of release as shown in Figure 3.

From Figure 3, it can be seen that on the first three days, both sample C and E had the same phosphorus release behaviour, but on the next day the amount of phosphorus in the soil in sample E was lower than that of sample C. Sample C was able to maintain more amount of phosphorus in the soil than that of sample E. According to the results, it can be stated that the slow release behaviour of coated fertilizer can be obtained by creating the dense surface with less pore on the matrix structure.



3.2. Swelling Analysis

Swelling analysis was done to determine the water absorption capacity of the coating system. Table 1 shows the results of swelling analysis for each variation of fertilizer coating.

Table 1. The swelling behaviour for different coating systems on fertilizer

Type of fertilizer	Starch content (%)	Chitosan : Starch ratio	Swelling (%)
A	1	100 : 0	24.658
B	1	70 : 30	24.735
C	1	30 : 70	18.422
D	1	70 : 30	25.099
E	2	70 : 30	18.917
F	3	70 : 30	20.282
G	-	-	7.828

When compared with non-coating fertilizer (sample G), it can be seen that the presence of coatings (sample A - F) increased the percentage of swelling. Increasing the swelling percentage affected the amount of water that can be absorbed by the coating film was also an increase. Table 1 shows that the presence of chitosan in coating system increased the percentage of swelling, where in samples A, B and D there was relatively more chitosan than starch. During the starch gelatinization process, the hydrophobic hydroxyl groups in the starch chain would lead to place on the outer side [6]. As a result of the condition, the more amount of starch content in the coating systems, the more hydrophobic the coating systems tend to be and the smaller the swelling percentage is.

The presence of starch in the coating systems was proven to have an effect on the reduction on swelling, but the physical strength of the coating was improved by increasing the chitosan content. The result is supported by the research of Xu, et al. [7], that films made from chitosan have poor water vapor barrier characteristics or high Water Vapor Transmission Rate (WVTR) compared to films that have been modified with starch. Water vapor barrier or Water Vapor Transmission Rate (WVTR) is a parameter that indicates whether or not a layer is penetrated by water. A high WVTR or poor water

vapor barrier indicates that chitosan films are easily passed by water vapor. In conclusion, the addition of starch will slow the release of phosphorus content because of reducing the ability of the coating to absorb water.

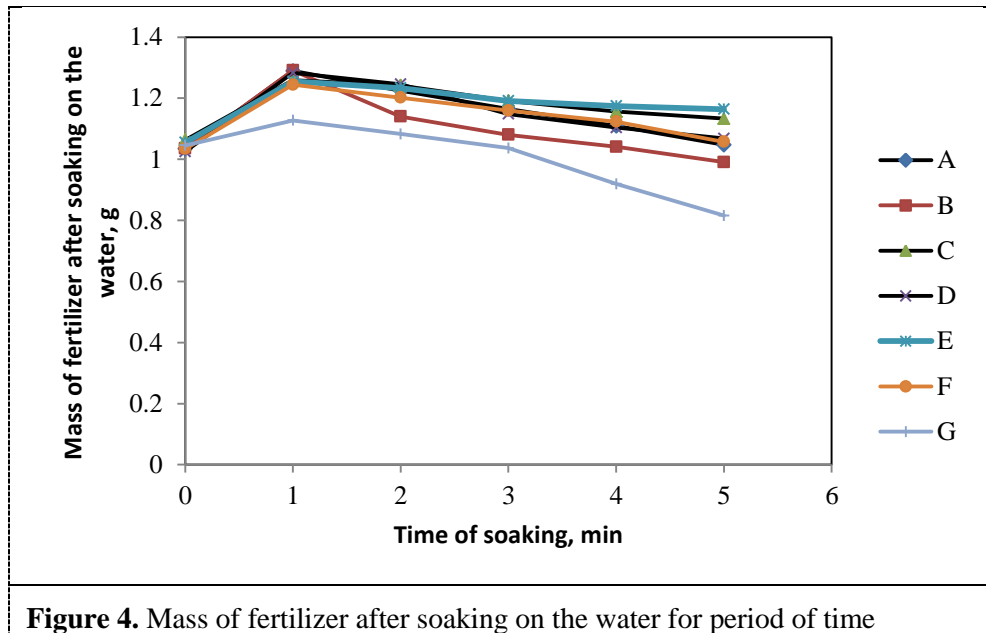


Figure 4 shows that the increase in fertilizer mass after soaking on the water had the maximum value in the first minute. It can be stated that the process of water absorption or swelling process of coated fertilizers occurred quickly. The phenomenon can be related that the phosphorus diffusion process out of fertilizer occurred slower and the phosphorus release process followed a diffusion controlled transport mechanism. If the swelling rate is much faster than that of the diffusion rate, the controlling mass transfer is the diffusion rate.

3.3. The Performance of Phosphorus Released by Coated Fertilizers

The release behaviour performance of coated fertilizer can be conducted by measuring the amount of phosphorus release in to the soil with a spectrophotometer.

Table 2 shows that the coated fertilizers had slower release behavior than that of non-coated fertilizers. The increasing amount of chitosan could produce the strong matrix of layer but gave more pores, otherwise the increasing amount of starch could enhance the hydrophobicity of coating system. The sample C gave the best performance as slow release fertilizer because it had the best physical properties as surface barrier to retain the phosphorus on the fertilizer. It can also be stated that the effect of the chitosan : starch ratio is greater to release behaviour than that of the starch content on coating system.

Table 2. The Amount of Phosphorus Release on to soil at different sample for period of release

Type of Fertilizer	Percentage of Phosphorus Content (%)						
	24 h	48 h	72 h	96 h	120 h	144 h	168 h
A	7.775	3.537	1.611	1.617	1.174	1.131	0.499
B	7.651	3.334	2.236	1.669	1.062	1.104	0.499
C	7.745	3.316	2.430	2.059	1.956	1.448	0.904
D	7.671	3.448	2.317	1.422	1.230	1.091	0.585
E	7.668	3.337	2.377	1.820	1.402	1.231	0.835
F	8.378	3.613	2.156	1.712	0.954	0.734	0.838
G	8.449	3.043	2.236	1.679	1.173	0.987	0.582

The results of this study can be compared with the research of Perez, J. and Francois, N. [8] who examined the behavior of nitrogen release in chitosan-starch coated fertilizers. The results of the study indicated that the higher amount of chitosan in the coating system, the more nitrogen can be released from fertilizer. At various chitosan : starch ratio 100:0; 30:70; and 20:80 nitrogen releases reached 95%, 73% and 80%, respectively. From this study it can be stated that the starch content for optimum performance is in the coating system which has composition chitosan:starch ratio as high as 30:70. The optimum coating is a coating which has the best physical properties so that the release of phosphorus is minimum.

4. Conclusions

The presence of chitosan on the coating system is responsible for producing a porous matrix surface while the availability of starch tends to reduce the number of pores in the surface. The swelling analysis shows that the presence of chitosan-starch coatings increases the water absorption ability. The greater the content of chitosan, the higher the percentage of swelling. The release behaviour analysis shows that the optimum of coated fertilizer is the fertilizer which has a mass ratio of chitosan:starch by 30:70, and starch concentration of 1%.

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